



Application of SLRP to Pearl Harbor Dredged Material

PURPOSE: The simplified laboratory runoff procedure (SLRP) was developed to provide U.S. Army Corps of Engineers Districts with a fast, inexpensive screening tool to assess potential surface runoff water quality problems resulting from the upland disposal of dredged material. The SLRP was applied to sediments from Indiana Harbor (Environmental Laboratory 1987), Blackrock Harbor, and the San Francisco Bay area during its development (Price, Skogerboe, and Lee 1998; Skogerboe 1995). Recently, SLRP was applied to New York Harbor sediment for the New York District and as part of the Long-Term Effects of Dredging Operations (LEDO) Program, Work Unit No. 33054, on a reimbursable basis. SLRP was also applied to Pearl Harbor sediment for the U.S. Navy on a reimbursable basis (Schroeder et al. 1999). This technical note summarizes the results and current application of SLRP in the decision-making process for Pearl Harbor.

BACKGROUND: The surface runoff water quality component of the technical and decision-making framework for the management of dredged materials (Lee et al. 1991, USACE/USEPA 1992) evaluates the potential water quality problems that may result from discharges of storm water from contaminated dredged material placed in upland environments. Water leaving an upland confined disposal facility (CDF) is regulated as a dredged material discharge and must receive state water quality certification. When dredged material is placed in a CDF, contaminant movement from the wet, unoxidized material will be mainly associated with suspended solids. As the material dries and oxidizes, suspended solids concentration may decrease, while contaminants such as heavy metals may become more soluble. The rainfall simulator lysimeter system (RSLS) predicts these effects so that restrictions and/or treatments, such as controlling movement of suspended solids or providing adequate mixing zones, can be incorporated into the CDF design.

The RSLS testing protocol for surface runoff water quality, described by Skogerboe, Price, and Brandon (1988), has been applied to dredged material from a number of locations including Indiana Harbor (Environmental Laboratory 1987), Black Rock Harbor (Skogerboe et al. 1987), New Bedford Harbor (Skogerboe, Price and Brandon 1988), Oakland Harbor (Lee et al. 1992a, 1992b, 1993a, 1993b), and others. Contaminants have included heavy metals, PAHs, PCBs, pesticides, organotins, and dioxins. The procedure uses a rainfall simulator/lysimeter system (RSLS) in the laboratory. Although the RSLS is an effective tool for predicting surface runoff water quality from upland CDF, the procedure is expensive, time-consuming, and can only be conducted at WES. A need for a faster, less expensive response to surface water quality concerns prompted the development of a simple laboratory procedure that could be performed by any qualified laboratory with widely available equipment. The SLRP is designed to provide a less-expensive, rapid response screening evaluation of surface runoff water quality from upland CDFs.

It is important to note that the SLRP currently has limited application, as the evaluation and interpretation of results is still in progress. The LEDO Surface Water Quality Work Unit ends in Fiscal Year 99. Field validation of the SLRP will proceed under the Dredging Operations and

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Environmental Research (DOER) Program, scheduled for Fiscal Year 2000. When completed, the SLRP will be incorporated into the technical framework as a Tier II type evaluation.

METHODS AND MATERIALS

Simplified Laboratory Runoff Procedure

Upon receipt, the two 19- ℓ polyethylene buckets of Pearl Harbor sediment were consolidated and thoroughly mixed with a lightning mixer to ensure homogeneity and samples were collected for the determination of sediment physical and chemical characteristics. The mixed sediment was placed back in the original buckets, sealed and stored in a walk-in cold room at 4 °C until needed. The SLRP requires the preparation of simulated runoff water using wet, unoxidized and dry, oxidized sediment in sediment-to-water ratios corresponding to the ranges of suspended solids concentrations measured in surface water runoff from previous RSLS studies. Ratios used for the Pearl Harbor sediment are shown in Table 1. Each ratio for the wet and dry procedures was replicated three times. For purposes of describing runoff water quality from CDFs, "total contaminants" refers to unfiltered samples and "dissolved" refers to filtered samples.

Table 1
Sediment-to-Water Ratios and Corresponding Suspended Solids Concentrations

Sediment Condition	1:20	1:200	1:2,000	1:20,000
Wet	50,000 mg ℓ^{-1}	5,000 mg ℓ^{-1}	500 mg ℓ^{-1}	—
Dry	—	5,000 mg ℓ^{-1}	500 mg ℓ^{-1}	50 mg ℓ^{-1}

- **Wet, Unoxidized Sediment.** The purpose of the wet portion of the SLRP is to simulate the quality of surface water leaving an upland CDF soon after filling with dredged material, particularly after dewatering when maximum surface exposure exists and movement of soil particles due to the impact of rainfall is high. This represents the worst case scenario for loss of contaminants bound to soil particles in runoff water at concentrations from 500 to 50,000 mg ℓ^{-1} . In a managed CDF, the release of suspended solids is controlled and concentrations of this magnitude would not be allowed. However, controlling suspended solids does not prevent the release of soluble contaminants that may be generated as a result of rain-induced suspension of sediment particles. Surface water released after settling of suspended solids may still contain elevated levels of soluble contaminants. For this reason, worst-case scenarios are evaluated. To accomplish this, wet, anaerobic sediment is simply diluted to prepare simulated runoff samples. After thorough mixing, sediment was removed from the bucket, placed in polycarbonate centrifuge bottles, and mixed with reverse osmosis (RO) water to the appropriate sediment-to-water ratios on a dry weight equivalent basis. The prepared samples were then placed on a mechanical shaker and agitated for 1 hr to ensure adequate suspension and dissolution of the sediment, as indicated in Figure 1. Half of the samples were divided into separate 1- ℓ glass bottles for PAHs and 500-ml nalgene bottles for metals and ammonia. Samples for metals and ammonia were acidified to less than pH 2.0 with nitric and sulfuric acid, respectively. These represent the total contaminants in unfiltered water. The other halves were centrifuged at 7,000 RPM ($8288 \times g$) and 15 °C for 10 min. The supernatant was decanted and filtered through a 0.45- μ m filter prior to placement in the

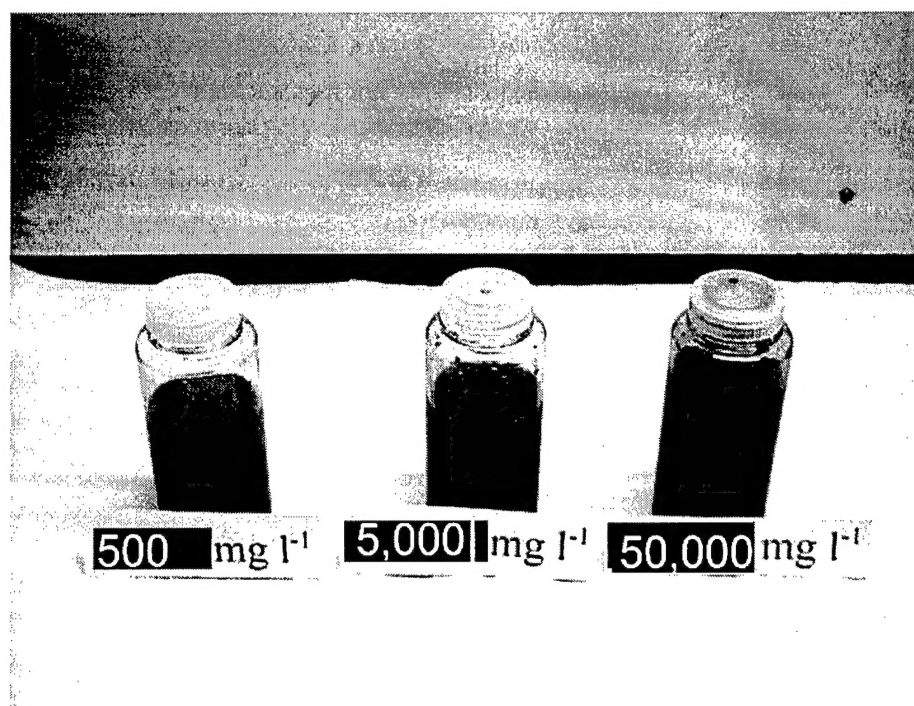


Figure 1. Suspended sediment in simulated runoff samples

proper containers and preservation with acid. These samples represent the dissolved contaminants in filtered water.

- **Dry, Unoxidized Sediment.** The purpose of the dry portion of the SLRP is to simulate the long-term effects of drying and oxidation of dredged material on movement of contaminants from an upland CDF. A single laboratory procedure, that can quickly simulate all the natural chemical, physical, and biological processes that occur as a dredged material dries and oxidizes, is simply not capable of accurately predicting the effects on all contaminants. The focal concern during the initial development of SLRP was heavy metals. Most heavy metals tend to have a greater tendency to become water soluble and exhibit higher rates of solubility as oxidation occurs. For this reason, sediment treatment procedures in SLRP were designed to maximize that effect as quickly as possible. Oxidation with hydrogen peroxide (H_2O_2) accomplishes this task as previously determined for Blackrock Harbor sediment (Price, Skogerboe, and Lee 1998) and San Francisco Bay sediments (Skogerboe 1995). Water quality results for the SLRP were similar to those obtained with the RSLS procedure.

Wet, unoxidized sediment was collected from the bucket and placed in a drying oven at 90°C for 48 hr. After drying was complete, H_2O_2 was added to rapidly oxidize the sediment, simulating long-term exposure to drying and exposure to oxygen. A pretest was necessary to determine the amount of H_2O_2 necessary to fully oxidize the Pearl Harbor sediment. Ten grams of oven-dried sediment was placed in a 3.8-l glass jar and 30-percent H_2O_2 was slowly and incrementally added each time, observing for an effervescent reaction (Figure 2). When the oxidation process was complete as indicated by lack of reaction, the amount of H_2O_2 used was recorded and the resulting H_2O_2 per gram of sediment was used in the SLRP

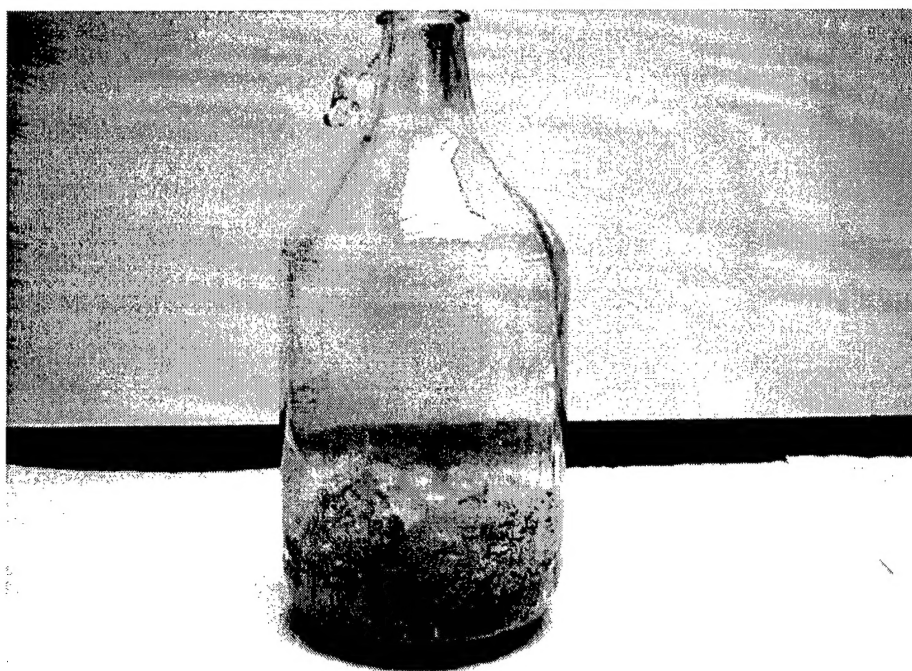


Figure 2. Oxidation of sediment with hydrogen peroxide

procedure. The oven-dried sediment was oxidized with H_2O_2 and then mixed with RO water to the sediment-to-water ratios indicated previously in Table 1. The samples were shaken overnight as described above and half of the samples were immediately placed in the appropriate sample containers. The remaining halves were then centrifuged and filtered as described for the wet sediment. Samples for both the wet and dry sediment were submitted for chemical analysis of As, Cd, Cr, Cu, Hg, Pb, Ni, Ag, Zn, PAHs, and NH_3 using the methods described by EPA (1986).

Screening Level Prediction of Surface Runoff Water Quality

The SLRP is designed to have nationwide application using a single procedure. To develop prediction capabilities, results of the SLRP are compared to results from an actual rainfall simulation using the RSLs in the laboratory. Multiple linear regression is used to develop prediction equations by relating the SLRP results to sediment sand content, sediment total organic carbon (TOC), and the results from the RSLs. Once this procedure has been applied to a sufficient number of sediments from various locations in the United States, analytical results of the extraction procedure can simply be fed into prediction equations for each contaminant. At this time, these prediction equations apply to only a few metals (As, Cd, Cr, Cu, Pb, and Zn) and only to Oakland Harbor, CA, sediments (Skogerboe 1995; Price, Skogerboe, and Lee 1998). Other sediments (New York Harbor and Blackrock Harbor) have since had the SLRP procedure applied with the RSLs. Data are currently being compiled for inclusion in the regression analysis and improvement to the prediction equations. However, equations will not be available for all contaminants due to the lack of useable analytical data.

The evaluation of surface runoff water quality from Pearl Harbor sediment did not include the RSLs procedure, so actual suspended solids concentrations during simulated rainfall events were not determined. If Pearl Harbor dredged material is placed in an upland environment, field validation of these results will be attempted, pending approval. The SLRP evaluates water quality using a range of expected suspended solids concentrations in the simulated runoff water. These ranges reflect the range of concentrations measured in previous studies, as indicated in Table 2. Suspended solids concentrations would be expected to be in the range of $5,000 \text{ mg } \ell^{-1}$ in surface runoff during the initial wet stage after filling CDF with Pearl harbor dredged material (with no managed retention of suspended solids). Once the material dries and forms a surface crust, suspended solids should fall to within the range of $500 \text{ mg } \ell^{-1}$. The SLRP addresses concentrations on an order of magnitude above and below these concentrations. Chemical data obtained from the SLRP (three replicates at each suspended solids concentration) were input into SigmaPlot® and regressions were plotted (95-percent confidence level) for total and dissolved contaminants from wet and dry sediment conditions. This indicates contaminant concentration in relation to suspended solids concentrations. Mean concentrations of dissolved contaminants were determined across the range of suspended solids relating to $18,500 \text{ mg } \ell^{-1}$ for wet sediment and $1,850$ for dry sediment. These values exceed suspended solids concentrations observed in most sediment previously tested in the RSLs procedure and results based on these suspended solids concentrations would be considered conservative in an unmanaged CPF. The dissolved constituents were compared to saltwater quality standards for the state of Hawaii. In the absence of state standards, it is assumed the EPA criteria for the protection of marine life (EPA 1987) would apply. Soluble contaminant concentrations that exceed the standards or criteria are reason for concern. A decision must then be made to either conduct quantitative testing using the RSLs procedure or design engineering controls based on the screening level results of the SLRP. Engineering controls may include surface runoff water treatment, mixing zones, and/or restricting runoff discharges.

Table 2 Suspended Solids Concentrations from Other Sediments Evaluated using the RSLs, $\text{mg } \ell^{-1}$		
Sediment	SS, Wet	SS, Dry
Indiana Harbor	6600	56
Blackrock Harbor	10326	167
Everett Harbor	6900	1000
New Bedford	7730	268
Oakland Inner	4447	1686
Oakland Upper	9140	970
Pinole Shoal	1500	618
West Richmond	3290	2340
Santa Fe Channel	6240	2130

RESULTS AND DISCUSSION

Surface Runoff from Wet Sediment

Analytical results of the SLRP-simulated runoff samples indicate that while the sediment is in a wet, unoxidized state, movement of metals will be associated with the suspended solids as most of the metals were not very soluble (Table 3). As long as the transported suspended solids remain in

a reduced state, increased solubility would not be expected. Only As and Ag exhibited significant solubility (as a percent of the unfiltered concentration) at 24 and 17 percent, respectively. However, levels of soluble As and Ag from the wet sediment were well below the water quality standards of 69 and 2.3 $\mu\text{g l}^{-1}$, respectively. None of the dissolved heavy metal concentrations exceeded the saltwater quality standards for the state of Hawaii even at the worst-case suspended solids load of 50,000 mg l^{-1} as shown in Figures 3-11. Regression lines for three replicates are plotted across three suspended solids concentrations for each sediment condition. Under storm events of 5.08 cm h^{-1} , suspended solids concentrations in runoff are expected to be closer to 5,000 mg l^{-1} , based on previous evaluations of surface runoff from freshly placed dredged material in a CDF as previously shown in Table 2. The SLRP does not currently predict the suspended solids concentrations for each sediment. Unknown variables in management practices (such as ponding or vegetation) will change the resulting suspended solids concentrations after a storm event. Instead, the surface runoff is evaluated across a wide range of suspended solids concentrations and the worst case scenario is considered. Regression lines exceeding the standard line at the highest suspended solids concentration (50,000 for wet dissolved and 5,000 for dry dissolved) are reason for concern.

Table 3
Solubility of Metals and Ammonia in Simulated Runoff, % of Total Unfiltered

Status	As	Cd	Cr	Cu	Pb	Hg	Ni	Ag	Zn	NH ₃
Wet	24	1.1	0.4	0.0001	0.3	0.6	0.2	17	0.0008	75
Dry	14	36	39	3.1	0.2	4.3	3.6	25	4.5	62

The analytical detection limit for NH₃ in this evaluation was 10 $\mu\text{g l}^{-1}$, equal to the saltwater standard. Dissolved NH₃ was not detected in simulated runoff from wet sediment at suspended solids concentrations of 500 and 5,000 mg l^{-1} . However, results for NH₃ indicate that during the

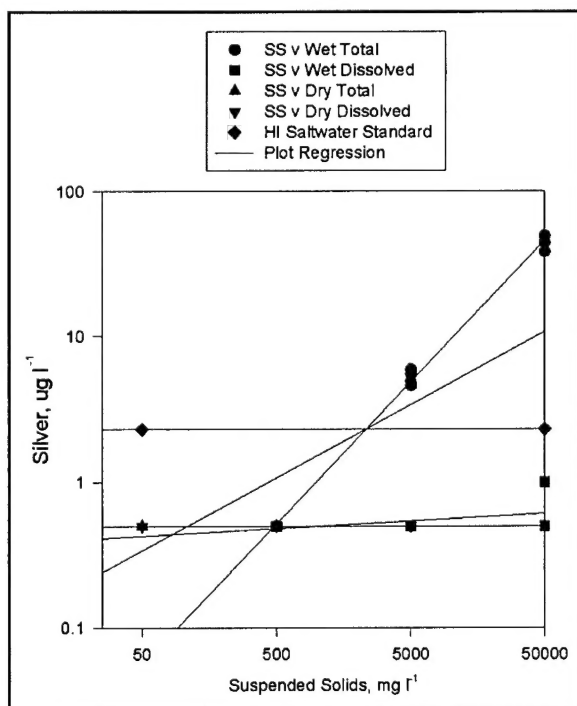


Figure 3. Silver in simulated runoff samples

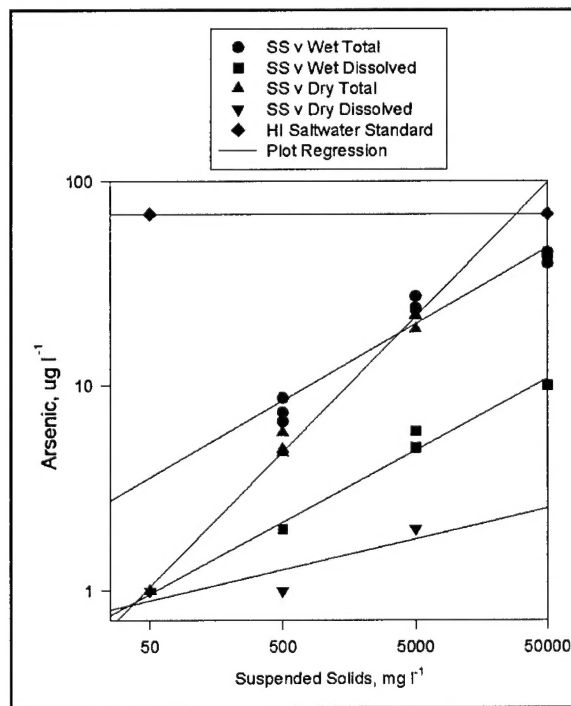


Figure 4. Arsenic in simulated runoff samples

wet stage, movement of NH_3 may be of concern, as indicated by the regression plot in Figure 12. Ammonia was very soluble (75 percent of total) in the wet stage and movement into receiving waters will exceed the 10 ug l^{-1} saltwater standard. As part of the reimbursable requirements for

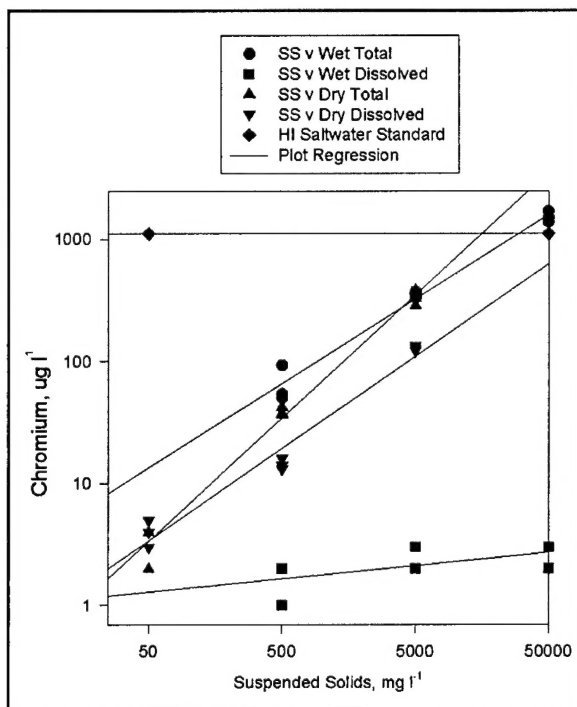


Figure 5. Chromium in simulated runoff samples

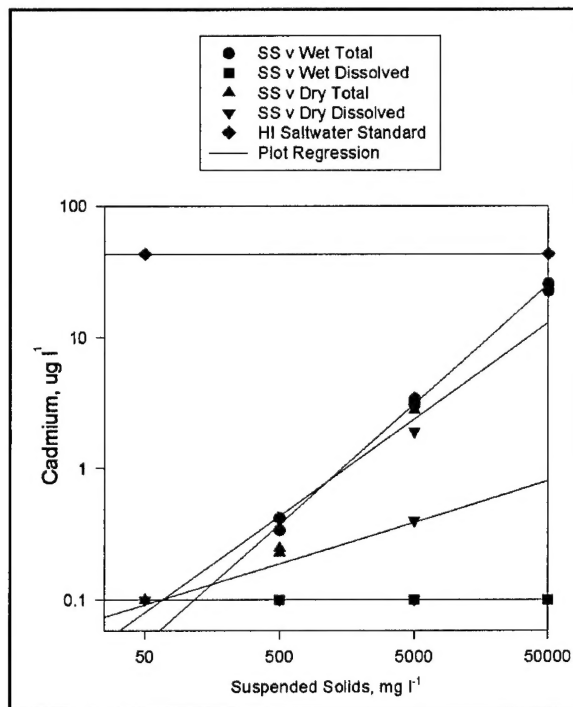


Figure 6. Cadmium in simulated runoff samples

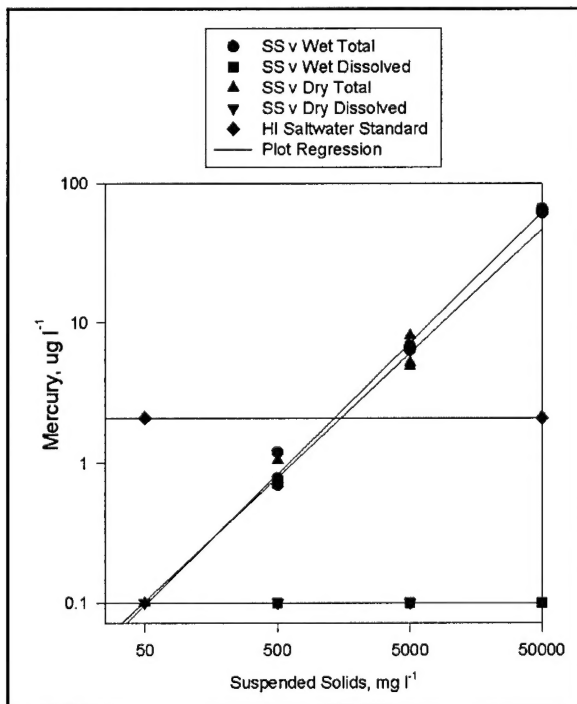


Figure 7. Mercury in simulated runoff samples

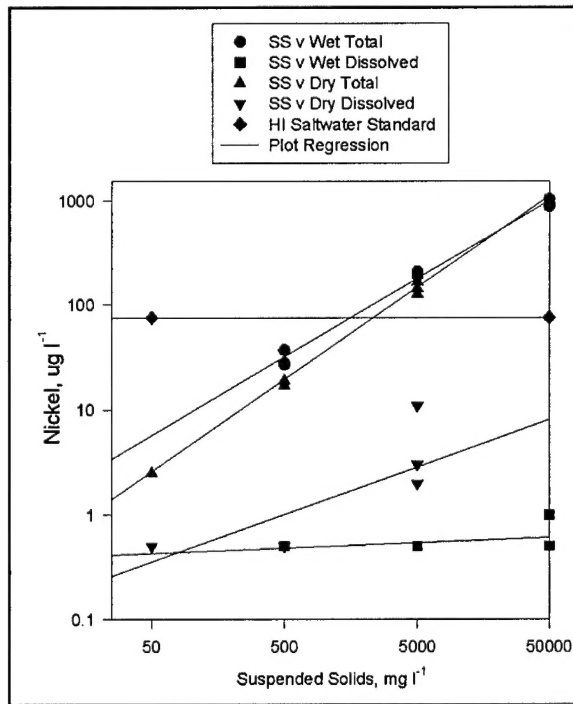


Figure 8. Nickel in simulated runoff samples

this project, the modified elutriate test was also performed on Pearl Harbor sediment (Schroeder et al. 1999). Results from the modified elutriate testing indicated that NH_3 concentrations in elutriate would be 1,450 and 1,510 $\mu\text{g l}^{-1}$ for total and soluble, respectively.

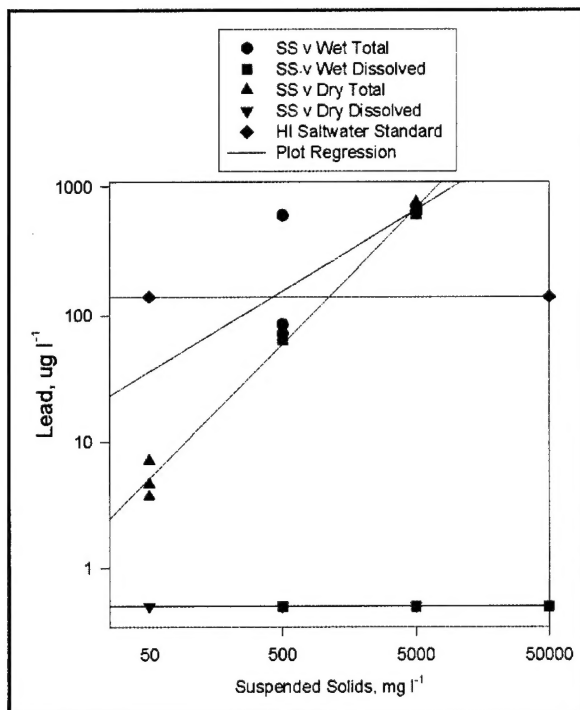


Figure 9. Lead in simulated runoff samples

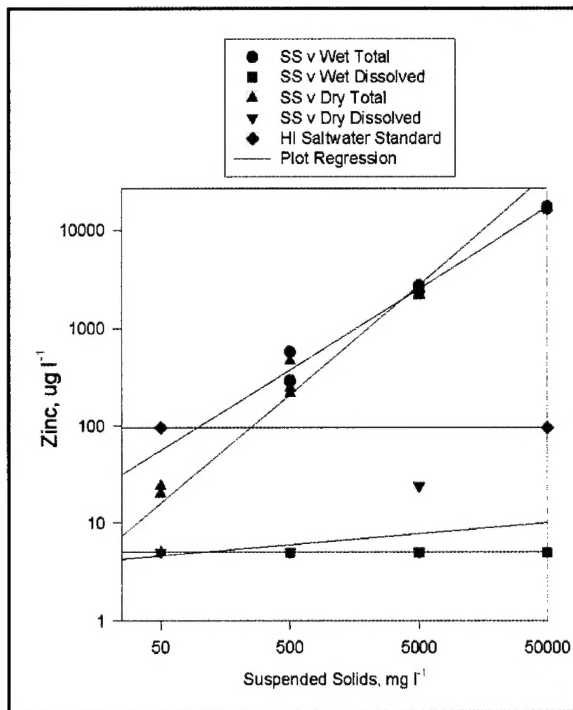


Figure 10. Zinc in simulated runoff samples

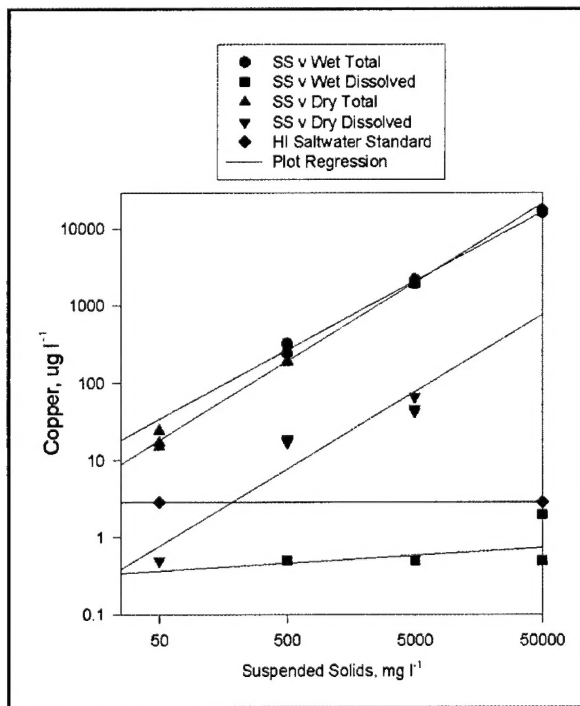


Figure 11. Copper in simulated runoff samples

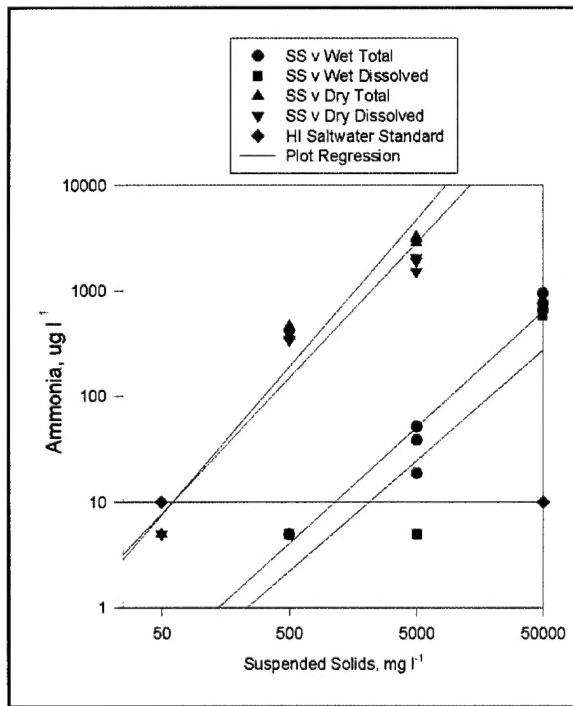


Figure 12. Ammonia in simulated runoff samples

Analytical results from the SLRP indicated PAHs in runoff water to be very limited. All of the detectable PAH analytes were associated with the suspended solids in the 5,000 to 50,000 mg ℓ^{-1} simulated runoff samples and no soluble PAHs were determined in the samples. Mean summation of the PAHs for each sediment condition and suspended solids concentrations were determined. Where at least one analyte was above detection limits, the remaining analytes were entered as half the detection limit value for summation purposes and the results are presented in Table 4. These results indicate that PAHs will not be a concern in runoff water.

Table 4
Summary of Total PAHs in Simulated Runoff Water, $\mu\text{g } \ell^{-1}$

Suspended Solids, $\text{mg } \ell^{-1}$	Wet Total	Wet Dissolved	Dry Total	Dry Dissolved
50,000	363.6	BDL ¹	NA ²	NA
5,000	89.7	BDL	BDL	BDL
500	BDL	BDL	BDL	BDL
50	NA	NA	BDL	BDL

¹ All PAH analytes were below method detection limits.

² Not applicable.

Surface Runoff from Dry Sediment

Drying and oxidation typically result in physicochemical changes to sediment. The effects of simulated drying and oxidation are shown in Table 5. As shown, drying and oxidation had little effect on pH, electrical conductivity (EC), and salinity. Although long-term drying and oxidation typically result in a reduction of sediment pH, the degree of reduction varies between sediments due to the various physicochemical characteristics. After 6 months of natural air drying in a soil lysimeter, pH values of Oakland, CA, Inner and Outer sediments were reduced from 7.97 to 6.88 and 8.11 to 7.02, respectively (Lee et al. 1992b). The pH of Blackrock Harbor sediment was reduced from 7.8 to 6.2 in the RSLs lysimeter over a 6-month period while long-term (1+ years) drying in the CDF reduced the pH from 7.5 to 4.7 (Skogerboe et al. 1987). The SLRP applied to Blackrock Harbor sediment indicated soluble metals were similar to the field results (Price, Skogerboe, and Lee 1998). Additional efforts to field validate the SLRP results will continue in the DOER Program.

Table 5
Effect of Oven Drying and H_2O_2 Treating on Pearl Harbor Sediment pH, EC, and % Moisture

Parameter	Wet	Oven Dry	H_2O_2 Treated
pH ¹	8.0	7.7	7.8
Moisture, (%) ²	192.1	NA	NA
EC, (mmhos cm^{-1}) ³	52.8	44.4	66.1
Salinity, (ppt) ⁴	38	33	36

¹ By 1:2 sediment to water ratio (Folsom et al. 1981).

² Oven-dry weight basis.

³ Saturated extracts using the method of Rhodes (1982).

⁴ Of above extracts on a hand-held refractometer.

The resulting soluble metals in runoff from the laboratory RSLs and RSLs applied in the CDF were not significantly different. Total metals should be reduced in runoff from dry sediment, as the suspended solids will be reduced. However, solubility of some metals will increase as the dredged

material is dried and oxidized. This was previously shown in Table 3. Solubility increased significantly for Cd, Cr, Cu, Hg, Ni, and Zn compared to solubility in runoff from wet sediment. However, as shown previously in Figures 5,6,7,8, and 10, soluble Cr, Cd, Hg, Ni, and Zn are predicted to be below the state of Hawaii saltwater quality standards as well as for Pb, Ag, and As (Figures 3, 5, and 6). After drying and oxidation, soluble Cu is predicted to exceed the state standard of 2.9 ug l^{-1} when suspended solids concentrations are in the 500 ug l^{-1} range and higher (Figure 11). Mean soluble Cu was 23.2 ug l^{-1} across the suspended solids range for the dry sediment, Table 6, nearly an order of magnitude above the standard.

Table 6 Mean SLRP Soluble Metals and Ammonia Concentrations and Water Quality Standards, ug l^{-1}			
Metal	Hawaii Saltwater Standard	Wet Dissolved	Dry Dissolved
As	69	6	1.3
Cd	43	0.1	0.4
Cr	1100	2.5	48.3
Cu	2.9	0.8	23.2 [†]
Pb	140	0.5	0.6
Hg	2.1	0.1	0.1
Ni	75	0.6	2
Ag	2.3	2.8	0.5
Zn	95	5	40
NH ₃	10	209	733
[†] Numbers in red exceed the Hawaii saltwater standard for filtered samples.			

Simulated drying and oxidation of Pearl Harbor sediment increased both total and soluble NH₃ in simulated runoff water samples compared to wet sediment (Figure 12). The dissolved NH₃ in surface runoff water from the dried, oxidized dredged material was predicted to significantly exceed the state saltwater quality standard of 10 ug l^{-1} . Mean concentrations of soluble NH₃ across the range of suspended solids concentrations was 733 ug l^{-1} or 73 times the state standard (Table 6). As a caution, one must note that the SLRP has not been previously applied to NH₃ and results may not be representative of actual field results. As the SLRP was designed and has been tested more for heavy metals, some SLRP conditions may give erroneous results for other contaminants. Oxidation with hydrogen peroxide may elevate NH₃ due to the release of organic nitrogen. In a natural oxidation process, one would expect the NH₃ to be reduced due to bacterial nitrification. Not all of these processes can be addressed in a single 'quick' test. Although the SLRP predicts elevation of NH₃ as the dredged material dries, this would not be expected in the field over a long period. Additional testing is required to verify the fate of NH₃ using the SLRP compared to actual RSLs tests and field results. However, as previously stated, the NH₃ concentrations determined by the modified elutriate test would be $1,510 \text{ ug l}^{-1}$, or 150 times the standard. A more restrictive effluent release or increased mixing zone would be required based on the results of the effluent test. Differences in the test procedures are designed to represent different conditions in the field and are expected to give different results.

The release of PAHs would not be a concern with dry Pearl Harbor dredged material. All PAHs in runoff from the dry, oxidized sediment were below the method detection limits and will not be a concern in surface water runoff from the dried, oxidized dredged material.

SUMMARY AND CONCLUSIONS: Surface water runoff is one of the pathways by which contaminants in dredged material may leave an upland disposal facility and impact receiving waters. Applying SLRP to Pearl Harbor dredged material indicates that heavy metals in rainfall-induced runoff from the wet unoxidized wet dredged material will be poorly soluble and bound to suspended particulates in the surface water runoff, as will PAHs. Soluble metals are not indicated to exceed state of Hawaii saltwater standards during this period. Retaining suspended solids will significantly restrict all movement of metals and PAHs from the upland disposal site. Assuming the higher level of suspended solids in runoff water, dissolved NH_3 will exceed the state standard for NH_3 in saltwater; however, this condition should not persist in a naturally oxidizing sediment. PAHs in surface runoff water were not soluble and were tightly bound to suspended solids. Total PAHs did not exceed a mean total of 363 ug l^{-1} in runoff water. Drying and oxidation of Pearl Harbor sediment significantly increased the solubility of most metals. However, only copper will exceed the state saltwater quality standard during dried conditions. The SLRP indicated that total and soluble ammonia increased as the sediment dried and oxidized. The accelerated release of ammonia by the rapid oxidation may be indicative of potential ammonia release. However, in natural field processes, the ammonia will be nitrified, presenting a degree of uncertainty concerning the predicted excessive ammonia levels in runoff after simulated long-term exposure of dredged material to oxidizing conditions. Additional research and field validation are required for ammonia and other contaminants for which data are inconclusive. Polyaromatic hydrocarbons were not detectable in runoff samples from dry sediment and should not be a concern.

Based on the results of the SLRP, mixing zone or discharge control will be required to reduce soluble ammonia while Pearl Harbor dredged material is in a wet unoxidized condition. As the material dries, the same requirement may be necessary for soluble copper. Typically, surface runoff pathway testing is conducted along with other pathway testing including the modified elutriate test (Palermo 1985). The two pathway tests complement each other and are required to assess the potential water quality problems resulting from two different water discharge processes. Results of the effluent pathway testing for Pearl Harbor (Schroeder et al. 1999) showed that ammonia, copper, and arsenic exceeded state water quality standards and would require discharge treatment or controls.

SLRP is being developed as a screening procedure to determine the need for more expensive evaluations of surface water runoff from dredged material using the RSLs. Many factors, such as vegetation, surface slope, ponding, extent of drying, etc., may dictate the quality of surface water runoff leaving an upland dredged material placement. The SLRP is designed to evaluate the worst case; maximum exposure of oxidized dredged material to significant rainfall events. Ideally, if a dredged material passes this test, then there should be no reason for restrictions on surface runoff water discharge. The SLRP was designed primarily for heavy metals, and with interpretive guidance, can be used for screening other contaminants. Additional evaluations will be conducted under the DOER Program to field verify results of both the SLRP and the RSLs to reduce uncertainties in interpretation. At this point, the SLRP is not a stand-alone evaluation and should not be used to make critical engineering design decisions. Where SLRP indicates failure of water quality standards, the RSLs may be required as a means of providing a more quantitative evaluation

of surface runoff water quality from the sediment in question. The SLRP results alone may lead to incorporating excessive and/or costly engineering controls and treatments in the final CDF design. If costly treatment or control measures are required or sensitive water quality issues are a concern as a result of SLRP results, the RSLs procedure is recommended.

Additional technical notes will follow including a technical note describing the SLRP testing procedure and application to New York Harbor sediment and comparison of the SLRP to the RSLs procedure.

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